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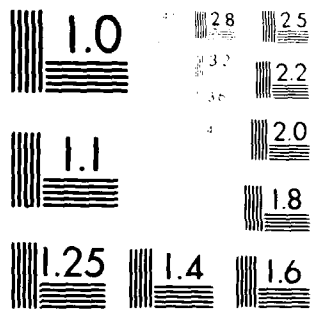
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LARGE HIGH QUALITY SINGLE CRYSTAL ALUMINUM PHOSPHATE FOR ACOUST--ETC(U)
JUN 80 T R AUCOIN, R O SAVAGE, M J WADE

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LARGE HIGH QUALITY SINGLE CRYSTAL ALUMINUM PHOSPHATE
FOR ACOUSTIC WAVE DEVICES

JUN 1980

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INTRODUCTION

Advanced military electronic warfare, secure communication, and surveillance/target acquisition systems such as mini-RPV's, REMBASS, and mortar and artillery locator radars, utilize a variety of acoustic wave devices. Typical are crystal oscillators, convolvers correlators, bulk and surface wave filters, resonators, delay lines, encoders, and decoders. High piezoelectric coupling, low acoustic loss (high Q), and temperature stability are critical requirements for materials to be used in the fabrication of next generation, high performance devices. Of the two crystals commonly used today, quartz exhibits temperature stability and low acoustic loss, while lithium niobate has relatively low loss and high coupling. α -AlPO₄ offers the highly desirable combination of all three.

Aluminum phosphate (α -AlPO₄), also known as the mineral Berlinite, recently emerged as a promising piezoelectric material for acoustic wave devices, offering one the unique combination of high electro-mechanical coupling with requisite temperature stability. Results of Chang and Barsch (1), O'Connell and Carr (2), and Ballato (3,4) show α -AlPO₄ to be an outstanding candidate for military signal processing applications.

AlPO₄ is in the same crystal class as quartz (Class 32) and similar geometric and physical properties are expected. Computed piezoelectric coupling factors based on the measurements of Chang and Barsch (1) translate into a large coupling advantage for α -AlPO₄.

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over α -quartz; up to 250% for bulk resonators and 400% for surface acoustic wave (SAW) devices as shown in Figures 1 and 2 for rotated y- cuts. This coupling factor advantage over quartz would be of little practical value, if it were not for the fact that AlPO_4 can be cut to have essentially zero temperature coefficients.

In projecting the use of a higher-coupling temperature stable material such as α - AlPO_4 in acoustic wave device applications, several advantages over existing materials are apparent. AlPO_4 devices would have lower insertion losses and eliminate the need for ovens to stabilize temperature when compared to quartz and lithium niobate components, respectively. One could then expect improved device performance and system reliability, as well as decreased acquisition cost and power consumption. However, the evaluation and testing of α - AlPO_4 in prototype components has been precluded by the poor quality and general unavailability of single crystals.

Alpha-aluminum phosphate generally crystallizes in a pseudo-hexagonal bipyramidal habit (Figure 3a) possessing no planes or center of symmetry but only axes of symmetry. The major and minor rhombohedra, r $\{10\bar{1}1\}$ and z $\{01\bar{1}1\}$, are predominant forms on α - AlPO_4 crystals. The major rhombohedron r is somewhat larger in size than the minor rhombohedron z. Prismatic m $\{10\bar{1}0\}$ faces are rarely encountered as contrasted to quartz (Figure 3b), and usually are not well developed.

α - AlPO_4 is isoelectronic and isostructural with α -quartz undergoing a phase transformation at approximately 584°C . Because of the severe strain, cracking, etc., which is created when cooling a crystal through a first order phase change, a low temperature growth technique is required. Standard hydrothermal growth techniques using saturated solutions of AlPO_4 in diluted phosphoric acid (H_3PO_4) have been used by several investigators (5-8) in Morey (9) type autoclaves at temperatures ranging from 150°C to 400°C . McBride and Hills (10) grew crystals from saturated solutions in sealed pyrex ampoules heated in a drying oven. In all articles published to date, actual crystal growth was obscured from the experimenter. However, the technique reported here (11) allows one to visually observe real time nucleation and growth kinetics. This feature has allowed, for the first time, precise determination of nucleation temperatures and optimum temperature-ramp rates for seeded solution growth. Using x-, y-, z-, and major (r) and minor (z) rhombohedral cuts for seed plates, large, high-optical-quality single crystals have been grown using this method.

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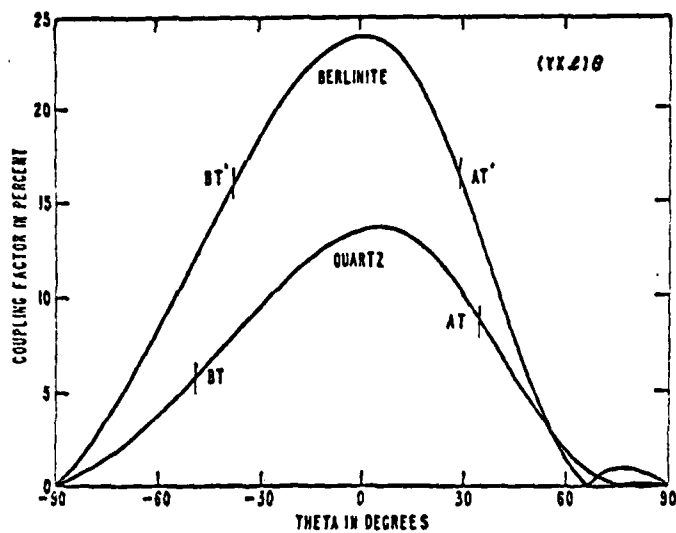


Figure 1. Coupling factor for α -quartz and α -AlPO₄.

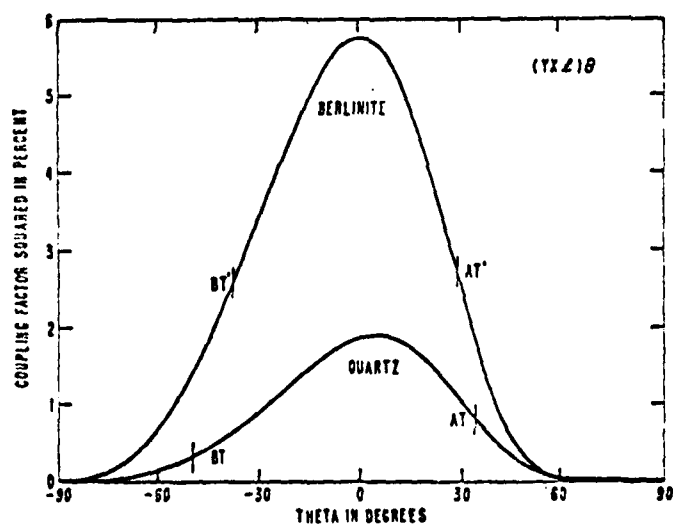


Figure 2. Coupling factor squared for α -quartz and α -AlPO₄.

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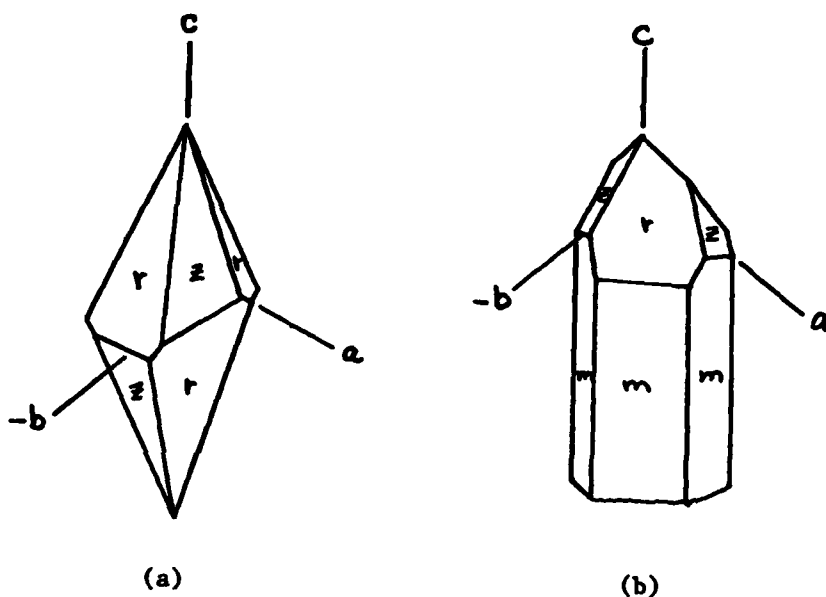


Figure 3. Frequently observed morphological habits of berlinite(a) and quartz(b).

EXPERIMENTAL

The solubility of $\alpha\text{-AlPO}_4$ in phosphoric acid decreases with increasing temperature as shown in Figure 4 from data by Stanley (5). Because of this retrograde solubility, two seeded methods are generally used to grow $\alpha\text{-AlPO}_4$: slowly increasing the temperature of a saturated solution; and mass transport from a nutrient feed in a reverse temperature gradient. The solubility of AlPO_4 in diluted phosphoric acid is greatly dependent on the acid concentration, increasing as the concentration increases. For example, at 175°C , 0.6 mole and 1.7 moles of AlPO_4 are soluble in one liter of 5.0 molar and 9.5 molar H_3PO_4 , respectively.

In attempting to obtain bulk crystals of high perfection, trial and error growth runs conducted in conventional hydrothermal autoclaves were found to be very time consuming. Little or no information was obtained relating to the origin of the growth defects observed in $\alpha\text{-AlPO}_4$ crystals, e.g., channeling, twinning, veiling, cracking, inclusions, etc. A hydrothermal growth system was designed and constructed (Figure 5) which allowed the direct observation of crystal formation during free nucleated and seeded growth. Growth processes

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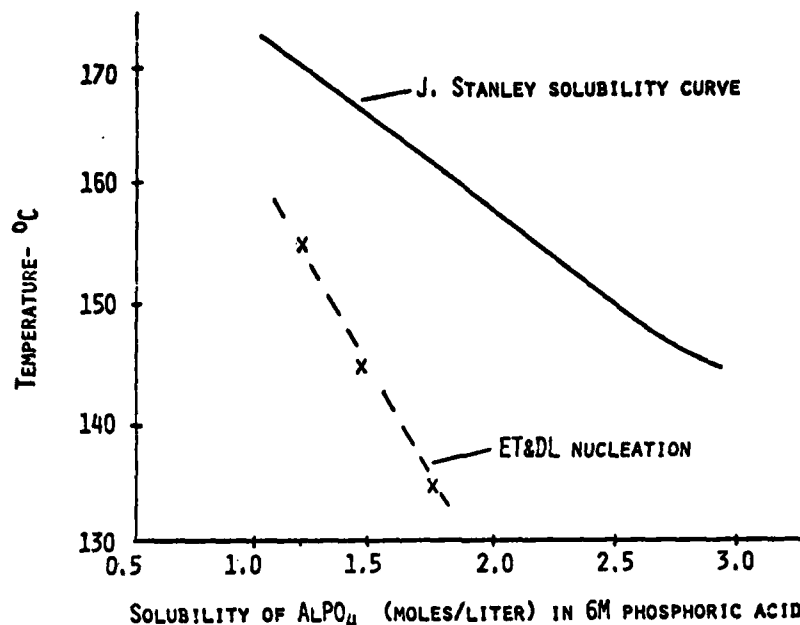


Figure 4. Solubility/nucleation of $\alpha\text{-AlPO}_4$ in 6M phosphoric acid.

such as etch-back, nucleation, veiling, cracking and surface roughening are all easily observable.

A Braun precision circulator, capable of maintaining temperatures at $\pm 0.004^\circ\text{C}$ to 250°C , was used to control the temperature of a silicone oil bath contained in a ten liter pyrex jar. This jar was placed in a larger pyrex container and the annular space filled with silicone oil for thermal insulation. Heavy wall quartz ampoules up to 3mm thick were selected for containment of growth solutions for several reasons: they are transparent; withstand vapor pressures to 200 psi or more; can be rapidly quenched without danger of explosion (runs must be quickly cooled and crystals removed due to the retrograde solubility of $\alpha\text{-AlPO}_4$ in H_3PO_4 as noted above); and can be hermetically sealed. The temperature of the growth solution was precisely programmed by increasing or decreasing the total resistance of the thermostat in the circulator. Ramp rates varying from 0.05°C to 3.5°C per day could be obtained by this technique.

Since high purity sources of AlPO_4 are not generally available, several approaches to obtaining satisfactory starting materials were explored. Our early growth runs were made from saturated solutions

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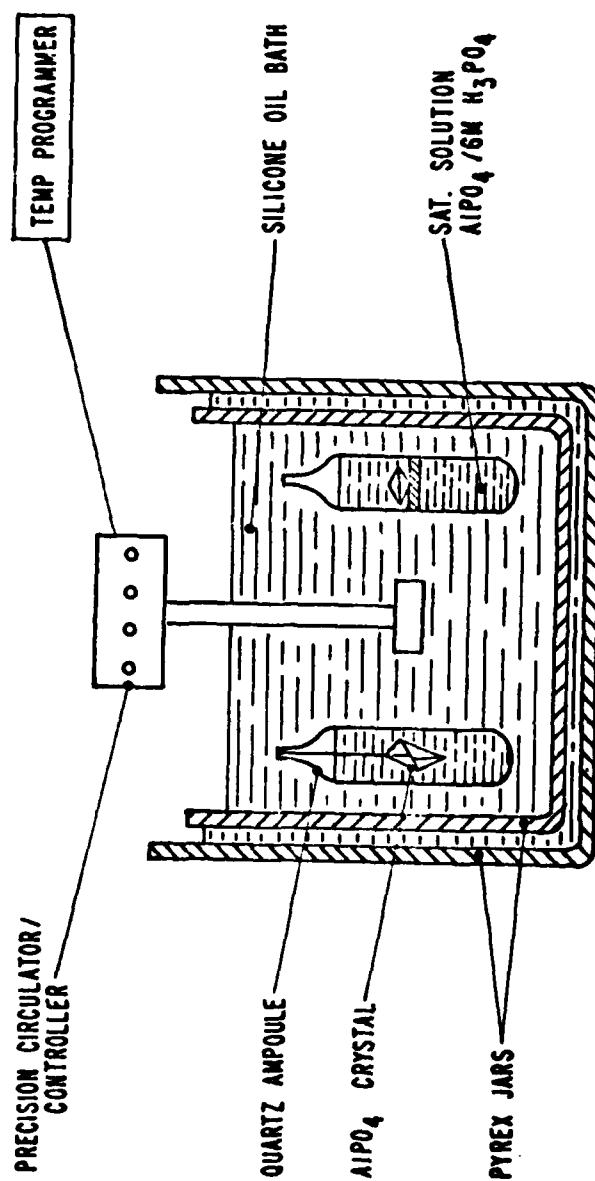


Figure 5. Modified hydrothermal system for direct observation of $\alpha\text{-AlPO}_4$ crystal growth.

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of twenty five year old Fisher purified AlPO_4 used by Stanley (5). Upon heating this material to $1,000^\circ\text{C}$ in air for one hour, a weight loss corresponding to two waters of hydration was observed. X-ray powder diffraction patterns taken before and after firing confirmed the Fisher material to be $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$. Reagent ACS grade H_3PO_4 was diluted with DI water to 6 molar strength and used to dissolve the AlPO_4 powder. As seen in Table I, atomic absorption analysis indicated that transition metal impurity levels were very low in these solutions.

In order to synthesize our own supply of high purity starting materials, the following approach was successfully used. De-ionized water was very slowly added to high purity phosphorus pentoxide (P_2O_5), having less than 3 ppm iron, to form H_3PO_4 . This reaction was very exothermic, requiring a water cooled refluxer to prevent vaporization losses. High purity aluminum (99.9999%) was then reacted with the acid to form an $\text{AlPO}_4/\text{H}_3\text{PO}_4$ solution. The amount of water, P_2O_5 , and aluminum was carefully calculated to yield a solution of the correct composition for crystal growth, e.g., 20 gms AlPO_4 per 100 ml of 6M H_3PO_4 . Solutions prepared by this technique contained approximately one-half the amount of iron and up to seventy times less chromium than the amounts found in the Fisher based solutions. See Table I.

The concentration of AlPO_4 in H_3PO_4 investigated during this study varied from 15 gms per 100 ml to 22.5 gms per 100 ml of acid. The onset of crystal growth (nucleation) was determined for each AlPO_4 concentration by carefully monitoring etch-back and growth initiation on oriented seed plates. The seeds were generally used as cut by a wire saw. In some cases, additional seed preparation such as alumina polishing or ammonium bifluoride etching was performed. The nucleation temperatures obtained for AlPO_4 concentrations of 15.0, 20.0, and 22.5 gms per 100 ml (1.23, 1.64, and 1.85 moles/liter respectively) of 6M H_3PO_4 are shown in Figure 4. Having established the nucleation temperature for several concentrations, the effect of varying temperature ramp rates from 0.1°C to 2.0°C per day on crystal perfection was investigated. The quality of the growing crystals could be directly observed as a function of the rate of temperature rise.

The quartz ampoules used for growth were filled to 80% of their volume with the desired solution and sealed with or without seed crystals. Up to eight ampoules could be placed in the previously described growth apparatus (Figure 5) at one time. Conventional hydrothermal systems would require eight separate pressure vessels for the same number of runs. Ampoules up to 5cm in diameter and 150 ml in volume were used with seed plates consisting of x, y, z, and major

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Atomic Absorption Analysis AlPO ₄ /6M H ₃ PO ₄ solutions				Emission Spec. Analysis α-AlPO ₄ crystals			
Element	Fisher ALPO-30	ET&DL HPALPO-1	ET&DL HPALPO-2	Fisher ALPO-30	Stanley -	ET&DL HPALPO-1	ET&DL HPALPO-2
Fe	10.3	5.3	6.0	10	50	10	10
Ti	0.4	0.6	0.4				
Cr	2.8	0.04	0.04				
Mn	0.37	0.15	0.14				
Ni	1.90	0.08	0.09	ND	ND	ND	ND
Cu	0.30	0.44	0.36				
Zn	1.90	0.57	1.17				
Co	0.02	0.03	0.02				
Si	-	-	-	50	50	50	100
Mg	-	-	-	1	1	1	5

ND - Not Detected

TABLE I. Atomic absorption and emission spectroscopic analysis of AlPO₄ solutions
and α-AlPO₄ crystals. (ppm by weight/Eagle-Picher)

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rhombohedral faces. The temperature of the system was raised from room temperature to a point several degrees below the nucleation temperature to effect a slight etch back of the seed plate prior to growth. The temperature was then slowly raised until the seed underwent a slightly opaque to transparent transition, indicating nucleation had occurred.

RESULTS/DISCUSSION

The key factor to our successful growth of high-optical-quality single crystals of α - AlPO_4 was the development of a visual, hydro-thermal growth system. The ability to observe real time seed etch-back, nucleation, and veil formation at the seed/crystal interface and in the bulk crystal, allowed us in a minimum number of runs to ascertain optimum growth conditions. Figure 6 shows two examples of α - AlPO_4 single crystals which were grown on free nucleated seed crystals suspended by 3 mil gold wires. A saturated solution consisting of 20 gms per 100 ml of 6M H_3PO_4 and an increasing temperature rate of 2°C per day was used. These conditions resulted in growth rates of approximately 15 mils per day along the c- axis. Upon inspection, one observes severe etching and precipitate formation on the as-grown faces. Inspection of interior of the crystals after polishing or immersion generally revealed scattering centers and some cracks.

Figure 7 shows three crystals grown from the same concentration solution as those in Figure 6 except the rate of temperature rise has been decreased to 0.25°C per day. High-optical-quality (scatter-free) single crystals can be routinely grown on x, y, z, and major and minor rhombohedral faces using these conditions. It is possible by careful initiation of growth to completely eliminate veil formation at the seed crystal interface. Growth rates along the c- axis on basal-cut seeds was approximately 7 mils per day. The resulting crystals had excellent optical and mechanical properties and could be cut in any crystallographic direction using a wire saw. Crystal plates could also be lapped and polished without evidence of cleavage and fracture.

Transition metal ions and in particular iron, are expected to be a source of acoustic loss in α - AlPO_4 . Chemical analysis of the ET&DL starting solutions (Table I) indicate both a low iron content ($\sim 10\text{ppm}$) and a very low level of other transition metal ions. Emission spectroscopic analysis of crystals grown from these solutions show the levels of iron to be $\sim 10 \text{ ppm}$, while silicon is on the order of 50 ppm except for HPA1PO-2 (100 ppm). The reason for the higher amount of silicon in HPA1PO-2 may be that this run was approximately twice as long as the others and leaching of the quartz ampoule has occurred.

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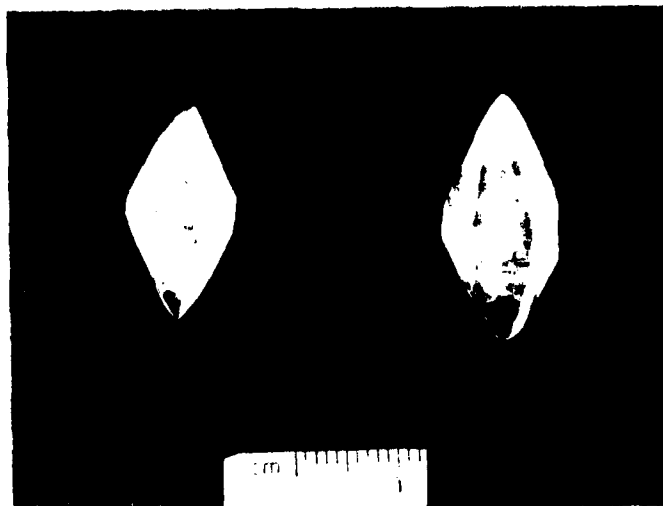


Figure 6. α -AlPO₄ crystals grown from 6M H₃PO₄ at 2° C/day temperature ramp rate.



Figure 7. α -AlPO₄ crystals grown from 6M H₃PO₄ at 0.25° C/day temperature ramp rate.

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Experiments are planned to investigate the effect of using teflon lined ampoules on silicon impurity level, now that the growth parameters have been established in our visual system.

Brazil or optical twinning is very common in α - AlPO_4 while Dauphiné or electrical twinning is encountered infrequently. Brazil twinning shows straight regular boundaries perpendicular to the y-axis, which are best detected by etching in saturated ammonium bifluoride solutions at room temperature, (Figure 8). In a Brazil twinned region the polarity of the x-axis is reversed. A consequence of extensive Brazil twinning in rotated y-cuts is a reduced or even zero piezoelectric coupling (12). The twinning behavior of α - AlPO_4 is similar to that of the amethyst variety of quartz. Amethyst almost always displays Brazil twinning and only rarely Dauphiné twinning. Since the Brazil twinning in amethyst is usually related to the iron content, it is possible that such twinning in α - AlPO_4 may also be impurity induced.



Figure 8. Reflection microphotograph of a Brazil twinned basal cut. The sample was etched in saturated ammonium bifluoride for 14 minutes at room temperature.

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SUMMARY

Recently there has been considerable interest in the potential for using single crystal AlPO_4 in a variety of acoustic wave applications. This interest was prompted by the possibility of obtaining simultaneously in one material, the properties of temperature stability, low acoustic loss, and high piezoelectric coupling. The poor quality and general lack of large AlPO_4 single crystals has precluded the evaluation and testing of this material in the desired prototype devices. This situation has motivated ~~the development of~~ a novel synthesis technique for attaining such crystals. ~~We have described~~ a unique modification (patent pending) of the conventional hydrothermal growth method which yields large ($>3\text{cm}$), high-optical-quality single crystals. The method permits continuous visual observation of the pressurized crystal growth process thus permitting close control of real-time nucleation and growth kinetics. The optimum conditions for attaining high quality crystals such as temperature-ramp rates, reagent concentration and purity, system design, and ampoule configuration ~~have~~ ^{are} ~~been presented.~~ These preliminary ~~very encouraging results have led~~ ^{are} ~~to a definition of the barrier to attaining low loss crystals as~~ being related to impurity content of the starting growth solutions and crystals, and Brazil type twinning. ~~Approaches to overcoming these problems have been delineated and are now being implemented.~~

ACKNOWLEDGEMENTS

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